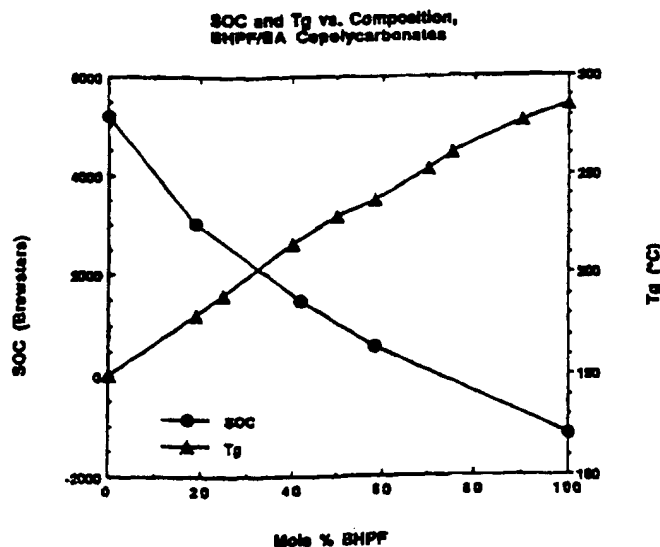




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08J 7/04, B05D 7/24 // C08G 64/16, G02F 1/13		A1	(11) International Publication Number: WO 97/13802
			(43) International Publication Date: 17 April 1997 (17.04.97)
(21) International Application Number: PCT/US96/16203 (22) International Filing Date: 11 October 1996 (11.10.96) (30) Priority Data: 60/005,153 13 October 1995 (13.10.95) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US). (72) Inventors: HU, Ing-feng; 6117 Londonberrie Court, Midland, MI 48640 (US). O'CONNOR, Paul, J.; 2814 Highbrook Drive, Midland, MI 48642 (US). TOU, James, C.; 1306 Foxwood Drive, Midland, MI 48642 (US). SEDON, James, H.; 195 Youngs Court, Midland, MI 48640 (US). BALES, Stephen, E.; 4409 Andre Street, Midland, MI 48642 (US). PERETTIE, Donald, J.; 3012 Travis Court, Midland, MI 48642 (US). (74) Agent: WILLIS, Reid, S.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: COATED PLASTIC SUBSTRATE



(57) Abstract

The present invention is a laminate which comprises: a) a plastic substrate having a surface; b) an adhesion promoter layer which is a first plasma polymerized organosilicon compound deposited on the surface of the substrate in the substantial absence of oxygen; and c) a protective coating layer which is a second plasma polymerized organosilicon compound deposited on the surface of the adhesion layer at a power density from 10^6 J/kg to 10^8 J/kg, and in the presence of a sufficient stoichiometric excess of oxygen to form a silicon polymer of $\text{SiO}_{1.8-2.4}\text{C}_{0.3-1.0}$ and $\text{H}_{0.7-4.0}$. The coating layer provides abrasion and solvent resistance for the substrate, and the adhesion promoter prevents the coating layer from peeling off the substrate. The coated plastic substrate can be used in liquid crystal display devices as an alternative to glass.

b) an adhesion promoter layer which is a plasma polymerized tetramethyldisiloxane deposited on the surface of the substrate in the substantial absence of oxygen, which adhesion promoter has a thickness of 1000 Å to 2000 Å;

5 c) a protective coating layer which is a plasma polymerized tetramethyldisiloxane deposited on the surface of the adhesion promoter layer at a power density from 10^6 J/kg to 10^8 J/kg, and in the presence of a sufficient stoichiometric excess of oxygen to form an organosilicon compound having the formula $\text{SiO}_{1.8-2.4} \text{C}_{0.3-1.0} \text{H}_{0.7-4.0}$ that contains trapped water and at least one of the following functional groups: -Si-O-Si-, -Si-CH₂-, -Si-H, or -Si-OH; wherein the thickness of the protective coating layer is not less than 0.1 micron and not greater than 2 microns; and

10 d) an SiO_x layer which is a layer of a plasma polymerized tetramethyldisiloxane deposited on the surface of the protective coating layer, in the presence of a stoichiometric excess of oxygen, and at a power density of at least four times the power density used to form the protective coating layer, wherein the SiO_x layer has a thickness of not less than 0.1 micron and not more than 1 micron.

15 The laminate of the present invention is resistant to abrasion and solvent by virtue of the presence of the layered coatings. Furthermore, the coatings are resistant to peeling by virtue of the presence of the adhesion promoter layer.

20 The substrate used for the laminate of the present invention can be a thermoplastic or thermoset material. Examples of suitable thermoplastic materials include polyethylene, polypropylene, polystyrene, polyvinylacetate, polyvinylalcohol, polyvinylacetal, polymethacrylate ester, polyacrylic acids, polyether, polyester, polycarbonate, cellulos resin, polyacrylonitrile, 25 polyamide, polyimide, polyvinylchloride, fluorine containing resins, and polysulfone. Examples of thermosets are epoxy and urea melamine.

30 The thickness of the substrate is application dependent, but is preferably not less than 0.1 mm, more preferably not less than 0.3 mm, and most preferably not less than 0.5 mm, and preferably not more than 10 mm, more preferably not more than 5 mm, and most preferably not more than 2 mm.

35 The surface of the substrate is coated first with an adhesion promoter layer, which is formed from the plasma polymerization of an organosilicon compound deposited on the surface of the substrate. The plasma polymerization of the organosilicon compound to produce the adhesion promoter layer is carried out at a sufficient power level to create an interfacial chemical reaction for adhesion, preferably at a power level from 5×10^7 J/kg to 5×10^9 J/kg. The adhesion promoter layer is prepared in the absence or substantial absence

COATED PLASTIC SUBSTRATE

The present invention is a coated plastic substrate, one embodiment of which may be useful in a liquid crystal display device. The coating protects the substrate against abrasion and solvent degradation.

Presently, there is a need for thinner, lighter weight liquid crystal displays with improved ruggedness. This need is manifested by the fact that an expensive portable device suffers catastrophic failure from the breakage of 10 cents worth of glass. Moreover, over half of all field failures from some devices are due to such breakage. Because of their superior flexibility and impact resistance, plastic substrates offer an alternative to glass for use as substrates in liquid crystal display devices (LCDs). Plastic substrates may also offer an economical advantage over glass substrates through improved yields in the manufacturing process.

The advantages inherent in glass substrates cannot be sacrificed for improved ruggedness, however. If plastics are going to be the substrate of choice, it is desirable that they be designed to have certain physical properties, including a) optical clarity; b) stability at temperatures required to process the display, typically at least 160°C; c) low birefringence; d) resistance to the chemicals used in display production; e) light stability; f) scratch resistance; g) hardness; and h) electrical resistivity.

Accordingly, it would be desirable to discover an alternative to glass for LCDs and other uses that overcomes the aforementioned deficiencies of glass substrates.

Figure 1 is a graph of stress optic coefficient (SOC) and glass transition temperature (T_g) of copolycarbonates of 9,9-bis(4-hydroxyphenyl)fluorene and bisphenol A.

In a first aspect, the present invention is a laminate which comprises:

- a) a plastic substrate having a surface;
- b) an adhesion promoter layer which is a first plasma polymerized organosilicon compound deposited on the surface of the substrate at a power level sufficient to create an interfacial chemical reaction for adhesion and in the substantial absence of oxygen; and
- c) a protective coating layer which is a second plasma polymerized organosilicon compound deposited on the surface of the adhesion layer at a power density from 10^6 J/kg to 10^8 J/kg, and in the presence of a higher level of oxygen than in step (b).

In a second aspect, the present invention is a laminate which comprises:

- a) a plastic substrate having a surface and a thickness of 0.1 mm to 10 mm;

diethoxydimethylsilane, methyltriethoxysilane, triethoxyvinylsilane, tetraethoxysilane, dimethoxymethylphenylsilane, phenyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, diethoxymethylphenylsilane, tris(2-methoxyethoxy)vinylsilane, phenyltriethoxysilane, and dimethoxydiphenylsilane. Examples of siloxanes include tetramethyldisiloxane (TMDSO) and hexamethyldisiloxane. Examples of silazanes include hexamethylsilazane and tetramethylsilazane.

The organosilicon polymer coatings are preferably applied by a plasma enhanced chemical vapor deposition (PECVD) technique as disclosed in U.S. Patent 5,298,587.

In one aspect of the present invention, the laminate is optically clear and comprises a substrate having a stress optic coefficient (SOC) in the range of from -2000 to +2500 Brewsters and a T_g , as determined by differential scanning calorimetry, preferably in the range of from 160°C to 270°C. Preferably, the SOC of the substrate is not less than -1000, more preferably not less than -500, and most preferably not less than -100, and not greater than 1000, more preferably not greater than 500, and most preferably not greater than 100 Brewsters. The T_g of the substrate is preferably not less than 180°C, more preferably not less than 190°C, and most preferably not less than 200°C, to not greater than 250°C, more preferably not greater than 240°C, and most preferably not greater than 230°C. The term "optically clear" is used herein to mean that the substrate has a measured total light transmission value according to ASTM D-1003 of at least 80 percent, preferably at least 85 percent.

For liquid crystal display applications, the substrate preferably comprises a carbonate polymer which can be a homopolymer or a copolymer or a blend having the desired SOC and T_g . Preferably, the substrate comprises a carbonate polymer which is the reaction product of an aromatic polyol, more preferably an aromatic diol, with a carbonate precursor. Representative examples of aromatic diols include catechol, hydroquinone, dihydroxynaphthalenes, dihydroxyanthracenes, bis(hydroxyaryl) fluorenes, dihydroxyphenanthrenes, dihydroxybiphenyls, and bis(hydroxyphenyl) propanes. Preferred aromatic diols include 9,9-bis(4-hydroxyphenyl)fluorene and bisphenol A.

Carbonate precursors suitable for use in preparing these carbonate polymers are well known in the art and include carbonic acid derivatives, phosgene, haloformates, or carbonate esters such as dimethyl carbonate or diphenyl carbonate. The carbonate polymers can be prepared by a variety of polymerization processes including interfacial, solution, or melt processes, all of which are well known in the art.

Preferably, the substrate comprises a carbonate polymer that contains repeat units of a dihydroxyarylfluorene monomer and a bisphenol monomer, more preferably 9,9'-dihydroxyarylfluorene and bisphenol A. The ratio of units of the 9,9'-dihydroxyarylfluorene

of a carrier gas such as oxygen. The term "substantial absence of oxygen" is used herein to mean that the amount of oxygen present in the plasma polymerization process is insufficient to oxidize all the silicon and carbon in the organosilicon compound. Similarly, the term "stoichiometric excess of oxygen" is used herein to mean that the total moles of oxygen present is greater than the total moles of the silicon and carbon in the organosilicon compound.

The thickness of the adhesion promoter layer is application dependent and is preferably not less than 50 Å, more preferably not less than 500 Å, and most preferably not less than 1000 Å, and preferably not more than 10,000 Å, more preferably not more than 5000 Å, and most preferably not more than 2000 Å.

The adhesion promoter layer is then coated with a protective coating layer which is a plasma polymerized organosilicon compound deposited on the surface of the adhesion promoter layer at a power density from 10^6 J/kg to 10^8 J/kg, and in the presence of a higher level of oxygen than used to form the adhesion promoter layer. Preferably, the protective coating layer is formed in the presence of a stoichiometric excess of oxygen.

The thickness of the protective coating for the substrate depends primarily on the properties of the coating as well as the substrate, but in general, is sufficiently thick to impart solvent resistance to the substrate. Preferably, the coating thickness is not less than 0.1, more preferably not less than 0.4, and most preferably not less than 0.8 micron, and not greater than 10, more preferably not greater than 5, and most preferably not greater than 2 microns.

The laminate may optionally comprise an SiO_x layer which is a plasma polymerized organosilicon compound deposited on the surface of the layer of the protective coating layer, in the presence of a stoichiometric excess of oxygen, and at a power density of at least twice, more preferably at least 4 times, and most preferably at least 6 times the power density used to form the protective coating layer. This layer is conveniently referred to as an SiO_x layer.

However, the SiO_x layer may also contain hydrogen and carbon atoms. The thickness of the SiO_x layer is generally less than the thickness of the protective coating layer, and is preferably not less than 0.01 micron, more preferably not less than 0.02 micron, and most preferably not less than 0.05 micron, and preferably not more than 5 microns, more preferably not more than 2 microns, and most preferably not more than 1 micron.

It may be desirable to coat the adhesion promoter layer with alternating layers of the protective coating layer and the SiO_x layer. The ratio of the thicknesses of the protective coating layers and the SiO_x layers are preferably not less than 1:1, more preferably not less than 2:1, and preferably not greater than 10:1, more preferably not greater than 5:1.

The organosilicon polymer coatings are prepared from an organosilicon compound such as a silane, siloxane, or a silazane. Examples of silanes include dimethoxydimethylsilane, methyltrimethoxysilane, tetramethoxysilane, methyltriethoxysilane,

syringe was removed and the reaction mixture was shaken for 30 seconds. A second addition of 50 percent NaOH (2.0 g, 25 mmole) was added by syringe through the septum.

The mixture was shaken for 1 minute, whereupon additional methylene chloride (11.17 g) was added by syringe followed by 4-dimethylamino pyridine (0.6 mL of a 1 percent aqueous solution). This mixture was shaken for 1 minute, whereupon the reactor was swirled in an ice bath. The reactor was opened, and the aqueous phase pipetted off. The organic phase was washed once with 1 N HCl and twice with water, and then removed by evaporation. The resultant copolycarbonate had a T_g of 230°C (PC-230). This general procedure was used to prepare additional quantities of copolycarbonate, which were injection molded into 127- x 127- x 1.6-mm plaques.

B. Preparation of a BHPF/BPA Copolycarbonate Blend

BHPF/BPA copolycarbonate blend having a T_g of 190°C (PC-190) was prepared by dry-blending the copolycarbonate prepared in the manner described in Part A (56 parts by weight) with bisphenol A polycarbonate (44 parts by weight). The resulting mixture was extrusion compounded and pelletized using a 30-mm Werner-Pfleiderer extruder with the feed zone set at 200°C and the four remaining zones set at 310°C.

C. Deposition of the PECVD coating on the Carbonate Polymer Substrates

The deposition of the highly crosslinked organosilicon coating (generally of the formula $\text{SiO}_x\text{C}_y\text{H}_z$) was carried out in a PECVD stainless steel box equipped with a shower head planar magnetron cathode as shown in Figures 1, 2, and 3 in U.S. Patent 5,320,875. A plaque from Part A or B (PC-230 or PC-190 respectively) was placed 3.2 cm above the cathode around the center of the cathode. The plaque was first coated with a 1000 to 1500 -Å thick adhesion layer of plasma polymerized TMDSO. TMDSO (4 sccm) was fed into the chamber through the shower head cathode. The gas inlet holes of the shower head were evenly distributed on the plasma ring of the magnetron cathode. This configuration of gas inlet maximized the decomposition probability of tetramethyldisiloxane by allowing the molecules to flow through the most intense plasma region. The TMDSO vapor flow was controlled by a Model 1152 MKS Inc. vapor flow controller and the plasma power was supplied by an ENI power supply (Model PlasmaLoc 2). The power loaded to the plasma during deposition of the adhesion promoter was 500 watts (W) at 40 KHz corresponding to a power density of 6.3×10^8 J/kg. The chamber base pressure was less than 1 mTorr. The process pressure was approximately 27 mTorr.

The highly crosslinked organosilicon coating was deposited onto the adhesion layer by feeding into the chamber a mixture of 40 sccm O_2 (flow rate controlled by Model 1160 MKS gas flow controllers) and 4 sccm TMDSO. The power loaded to the plasma during deposition was 40 W at 40 KHz, corresponding to a power density of 2.9×10^7 J/kg.

and bisphenol A is preferably not less than 30:70, more preferably not less than 40:60, and preferably not greater than 90:10, more preferably not greater than 70:30.

Figure 1 shows a graphical depiction of the variance of SOC and T_g of a number copolycarbonates of 9,9-bishydroxyphenylfluorene (BHPF) and bisphenol A (BPA). The graph indicates that copolycarbonates in the range of 30:70 to 90:10 mol percent BHPF/BPA have SOC's and T_g 's that are especially suitable for liquid crystal display device applications. The optimal SOC (SOC equals 0) occurs with a BHPF/BPA ratio of 70:30, whereas the optimal T_g occurs at a somewhat lower ratio. Fortunately, adjustment of T_g can be made without substantial change to the SOC, for example, by incorporating ester units into the carbonate polymer to make a carbonate/ester copolymer, or by blending polyesters and/or carbonate/ester copolymers with the carbonate polymer. This concentration of ester units incorporated into the carbonate polymer, or the amount of polyesters and/or carbonate/ester copolymers blended with the carbonate polymer, is sufficient to achieve the desired T_g without substantial diminution of other physical properties.

Preferably, the ester units are the reaction product of aliphatic or aromatic diacid or diacid chloride. The aliphatic diacid or diacid chloride is preferably a C_{3-12} diacid or di(acid chloride), more preferably a C_{4-8} diacid or di(acid chloride), and most preferably adipic acid, adipoyl chloride, succinic acid, or succinyl chloride. The aromatic diacid is preferably terephthalic acid, terephthaloyl chloride, isophthalic acid, isophthaloyl chloride, 2,6-naphthalene dicarboxylic acid, or 2,6-naphthalene diacid chloride. Preferably, the concentration of ester units in the substrate is in the range of from 10 to 50 mol percent, based on the total moles of carbonate units and ester units.

The following examples are for illustrative purposes only and are not intended to limit the scope of this invention. All percentages are weight:weight unless otherwise noted.

Example 1 -- Preparation of a $SiO_xC_yH_z$ -Coated Carbonate Polymer

A. Preparation of a 60:40 Mole Ratio BHPF/BPA Copolycarbonate

A copolycarbonate of 60 mole percent 9,9-bis(4-hydroxyphenyl) fluorene (BHPF) and 40 mole percent bisphenol A (BPA) was prepared as follows. To a 100 mL high pressure reactor with plug were added BPA (0.913 g, 4.0 mmole), BHPF (2.102 g, 6.0 mmole), t-butylphenol (0.045 g, 0.30 mmole), aqueous 50 percent NaOH solution (2.0 g, 25.0 mmole), and water (16.14 g). The reactor was purged with nitrogen. Nitrogen gas was blown through the air space of the reactor for 10 minutes, then the plug was tightened down. The sealed reactor was placed in a water bath (69°C to 71°C) and the solution was stirred. After the monomer was dissolved, phosgene solution in methylene chloride (20.08 g of 6.65 percent solution, 13 mmole) was added to the stirred mixture using a 25-mL gas-tight syringe. The

CLAIMS:

1. A laminate which comprises:
 - a) a plastic substrate having a surface;
 - b) an adhesion promoter layer which is a first plasma polymerized organosilicon compound deposited on the surface of the substrate at a power level sufficient to create an interfacial chemical reaction for adhesion and in the substantial absence of oxygen; and
 - c) a protective coating layer which is layer of a second plasma polymerized organosilicon compound deposited on the surface of the adhesion layer at a power density from 10^6 J/kg to 10^8 J/kg, and in the presence of a higher level of oxygen than used in step (b).
2. The laminate of Claim 1 which further comprises an SiO_x layer which is a plasma polymerized third organosilicon compound deposited on the surface of the layer of the protective coating layer, in the presence of a stoichiometric excess of oxygen, and at a power density of at least twice the power density used to form the protective coating layer.
3. The laminate of Claim 2 which further comprises alternating layers of the protective coating layer and the SiO_x layer.
4. The laminate of any of Claims 1 to 3 wherein the organosilicon polymers that are plasma polymerized are each independently selected from the group consisting of dimethoxydimethylsilane, methyltrimethoxysilane, tetramethoxysilane, methyltriethoxysilane, diethoxydimethylsilane, methyltriethoxysilane, triethoxyvinylsilane, tetraethoxysilane, dimethoxymethylphenylsilane, phenyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, diethoxymethylphenylsilane, tris(2-methoxyethoxy)vinylsilane, phenyltriethoxysilane, dimethoxydiphenylsilane, tetramethyldisiloxane, hexamethyldisiloxane, hexamethylsilazane, and tetramethylsilazane.
5. The laminate of any of Claims 1 to 4 wherein the organosilicon polymers that are plasma polymerized are each tetramethyldisiloxane.
6. The laminate of any of Claims 1 to 5 wherein the substrate is a carbonate polymer which comprises repeat units of a reaction product of a carbonate precursor with an aromatic diol.
7. The laminate of Claim 6 wherein the aromatic diol comprises resorcinol, catechol, hydroquinone, a dihydroxynaphthalene, a dihydroxyanthracene, a bis(hydroxyaryl) fluorene, a dihydroxyphenanthrene, a dihydroxybiphenyl, or a bis(hydroxyphenyl) propane.
8. The laminate of Claim 7 wherein the ratio of the repeat units of 9,9-bis(4-hydroxyphenyl)fluorene and bisphenol A is from 40:60 to 70:30.

Resistance of the coated plaques to N-methylpyrrolidinone (NMP) was determined by adding a drop of NMP to the coated surface and allowing the drop to stand for five minutes before rinsing it off with water. Visual observation of an absence of clouding showed a resistance to NMP. For PC-230, coatings of 1.0-, 1.2-, 1.4-, and 1.6-micron thickness impart solvent resistance. For PC-190, coatings of 1.2-, 1.4-, and 1.6-micron thickness impart solvent resistance.

Example 2 -- Preparation of a $\text{SiO}_x\text{C}_y\text{H}_z/\text{SiO}_x$ -Coated Carbonate Polymer

A plaque (either PC-190 or PC-230) with a layer of adhesion promoter was prepared in Example 1 was coated alternately with SiO_x and organosilicon coatings. The SiO_x coatings each had a thickness of 0.072 micron and the highly crosslinked organosilicon coatings each had a thickness of 0.262 micron. The first SiO_x coating was applied to the plaque by feeding into the chamber a mixture of 40 sccm O_2 (flow rate controlled by Model 1160 MKS gas flow controllers) and 4 sccm TMDSO. The power loaded to the plasma during deposition was 250 W at 40 KHz, corresponding to a power density of 1.8×10^8 J/kg. Then, the first organosilicon coating was applied using the conditions described in Example 1. The second SiO_x coating was applied, followed by a second organosilicon coating, then a third SiO_x coating, and finally a third organosilicon coating. The total thickness of the coatings was 1.0 micron. Both PC-190 and PC-230 samples were resistant to NMP with this alternate coating technique.

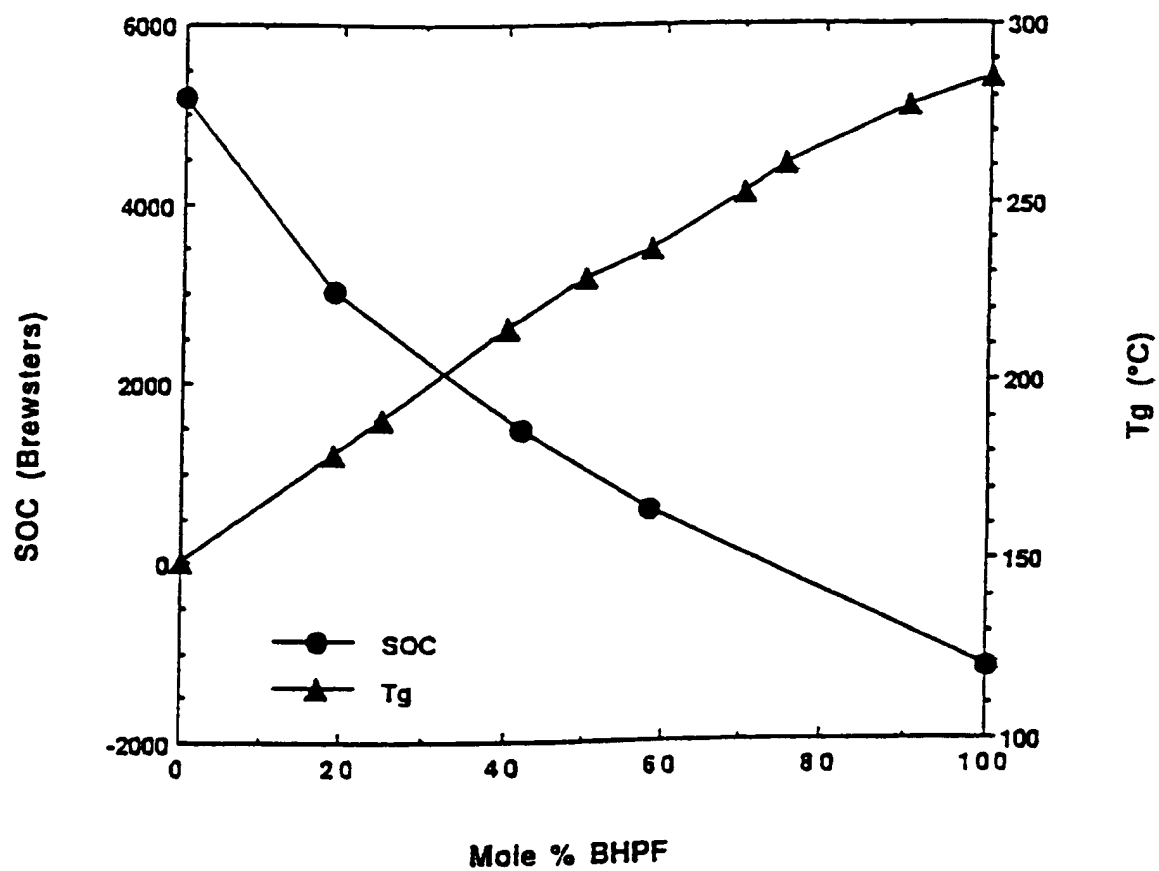
9. The laminate of any of Claims 1 to 7 wherein the T_g of the substrate is not less than 180°C and not greater than 240°C, and the SOC of the laminate is not less than -1000 Brewsters and not greater than 1000 Brewsters, which laminate is optically clear.

10. A laminate which comprises:

- 5 a) a plastic substrate having a surface and a thickness of not less than 0.1 mm and not more than 10 mm;
- b) an adhesion promoter layer which is a plasma polymerized tetramethyldisiloxane deposited on the surface of the substrate in the substantial absence of oxygen, which adhesion promoter has a thickness of not less than
- 10 1000 Å and not more than 2000 Å;
- c) a protective coating layer which is a plasma polymerized tetramethyldisiloxane deposited on the surface of the adhesion promoter layer at a power density from 10^6 J/kg to 10^8 J/kg in the presence of a sufficient stoichiometric excess of oxygen with respect to tetramethyldisiloxane to form an organosilicon compound
- 15 having the formula $\text{SiO}_{1.8-2.4} \text{C}_{0.3-1.0} \text{H}_{0.7-4.0}$ that contains trapped water and at least one of the following functional groups: -Si-O-Si-, -Si-CH₂-, -Si-H, or -Si-OH; wherein the thickness of the protective coating layer is not less than 0.1 micron and not greater than 2 microns; and
- 20 d) an SiO_x layer which is a layer of a plasma polymerized tetramethyldisiloxane deposited on the surface of the protective coating layer, in the presence of a stoichiometric excess of oxygen, and at a power density of at least four times the power density used to form the protective coating layer, wherein the SiO_x layer has a thickness of not less than 0.1 micron and not greater than 1 micron.

FIG. 1

SOC and Tg vs. Composition,
BHPF/BA Copolycarbonates



INTERNATIONAL SEARCH REPORT

International Application No
PL/US 96/16203

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08J/04 B05D7/24 //C08G64/16,G02F1/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 830 873 (G. BENZ ET AL.) 16 May 1989	1-7,9,10
Y	see claims 1-7,11 see column 3, line 12-32 see column 3, line 62 - column 4, line 3; figure 1 see column 4, line 4-34 see column 4, line 53 - column 5, line 29 ---	1-7,9,10
Y	US,A,5 320 875 (I.F.HU ET AL.) 14 June 1994 see claim 1 see column 1, line 66 - column 2, line 16 see column 8, line 19-26 see examples 7,8 ---	1-7,9,10
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another claim or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

Date of the actual completion of the international search

15 January 1997

Date of mailing of the international search report

26.03.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Hallemeesch, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/16203

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US-A-4830873	16-05-89	DE-A-	3413019	17-10-85
		WO-A-	8504601	24-10-85
		EP-A-	0177517	16-04-86
		JP-B-	6011806	16-02-94
		JP-T-	61501781	21-08-86

US-A-5320875	14-06-94	US-A-	5298587	29-03-94
		US-A-	5433786	18-07-95
		US-A-	5494712	27-02-96
		CA-A-	2147486	07-07-94
		EP-A-	0674722	04-10-95
		JP-T-	8505186	04-06-96
		WO-A-	9414998	07-07-94
